



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Tsukasa Fujieda ) Group Art Unit:  
Appl. No.: 10/576,193 ) 1711  
 )  
Filed: April 17, 2006 ) Examiner:  
 ) Robert Walters, Jr.  
For: METHOD OF FORMING LUSTER )  
COATING FILM )

---

DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents  
PO Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

I, Tsukasa Fujieda do hereby declare that:

1. I am one of the inventors of the above-identified application.
2. I graduated from Kobe Design University, Faculty of Design, Department of Visual Communication Design in March 1993. In April 1993, I joined KANSAI PAINT CO., LTD., assignee of the above-identified application, where I was engaged in research on color development

from April 1993 to the present. Since April 1994, I have been engaged in research on color development as an engineer in the CD laboratory of KANSAI PAINT CO., LTD.

3. The experiments given below were carried out under my general direction and supervision.

### Experiment

#### 1. Summary and Purpose of Experiment

A method comprising repeating a step of applying a base coating composition and a step of applying a clear coating composition, and a method in which each of the above steps is not repeated, are conducted with a variety of thicknesses of the base coating composition applied, and with a variety of the number of stages of applying the base coating composition. Each of the obtained coating films was evaluated for density of texture and flip-flop property.

In each example, parts and percentages are by weight.

#### 2. Experimental Methods

Preparation of aqueous luster thermosetting base coating composition and clear coating composition

Aqueous luster thermosetting base coating composition (A-

2)

Production Example 1

(Production of acrylic resin emulsion)

One hundred and thirty parts by mass of deionized water and 0.52 parts by mass of Aqualon KH-10 (tradename, surfactant, produced by Dai-Ichi Kogyo Seiyaku Co., Ltd.) were placed in a reactor equipped with a thermometer, a thermostat, a stirrer, a reflux condenser, and a dropping device, and mixed by stirring under a nitrogen stream; afterward, the resulting mixture was heated to 80°C. Subsequently, 1% out of the total amount of the monomer emulsion (1) shown below and 5.3 parts by mass of 6% aqueous ammonium persulfate solution were introduced in the reactor, and maintained at 80°C for 15 minutes. Thereafter, the remaining monomer emulsion (1) was added dropwise to the reactor maintained at the same temperature over 3 hours. After addition, the resulting mixture was aged for 1 hour. Further, the monomer emulsion (2) shown below was added dropwise to the reactor over 1 hour, and the resulting mixture was aged for 1 hour. Then, the mixture was cooled to 30°C while 40 parts by mass of 5% aqueous dimethylethanolamine solution was gradually added to the reactor, and the resulting product was filtered and discharged through 100-mesh nylon cloth. Thereby, an acrylic resin emulsion with a mean particle diameter of 100 nm (measured by diluting the filtrate with deionized

water, and using a "COULTER N4" submicron particle size distribution analyzer (produced by Beckman Coulter, Inc.) at 20°C), and a solids concentration of 30% was obtained. The acrylic resin had an acid value of 33 mgKOH/g and a hydroxy value of 25 mgKOH/g.

Monomer emulsion (1): a monomer emulsion obtained by mixing and stirring 42 parts by mass of deionized water, 0.72 parts by mass of Aqualon KH-10, 2.1 parts by mass of methylenebis acrylamide, 2.8 parts by mass of styrene, 16.1 parts by mass of methyl methacrylate, 28 parts by mass of ethyl acrylate, and 21 parts by mass of n-butyl acrylate.

Monomer emulsion (2): a monomer emulsion obtained by mixing and stirring 18 parts by mass of deionized water, 0.31 parts by mass of Aqualon KH-10, 0.03 parts by mass of ammonium persulfate, 5.1 parts by mass of methacrylic acid, 5.1 parts by mass of 2-hydroxyethyl acrylate, 3 parts by mass of styrene, 6 parts by mass of methyl methacrylate, 1.8 parts by mass of ethyl acrylate, and 9 parts by mass of n-butyl acrylate.

#### Production Example 2

(Production of polyester resin)

One hundred and nine parts by mass of trimethylolpropane, 141 parts by mass of 1,6-hexanediol, 126 parts by mass of hexahydro phthalic anhydride, and 120

parts by mass of adipic acid were placed in a reactor equipped with a thermometer, a thermostat, a stirrer, a reflux condenser, and a water separator. After the mixture was heated in such a manner that the time taken for increasing the temperature from 160°C to 230°C was 3 hours, a condensation reaction was carried out at 230°C for 4 hours. Subsequently, in order to add carboxy to the resulting condensation reaction product, 38.3 parts by mass of trimellitic anhydride was added, and a reaction was carried out for 30 minutes at 170°C. Then, the reaction product was diluted with 2-ethyl-1-hexanol to thereby obtain a polyester resin solution having a solids concentration of 70%. The obtained polyester resin had an acid value of 46 mgKOH/g, a hydroxy value of 150 mgKOH/g, and a weight average molecular weight of 6,400. The term "weight average molecular weight" used herein refers to a value measured using the calibration curve of standard polystyrene by gel permeation chromatography (GPC).

(Production of aqueous luster thermosetting base coating composition (A-2))

#### Production Example 3

One hundred parts of the acrylic resin emulsion obtained in Production Example 1, 57.1 parts of the polyester resin solution obtained in Production Example 2, and 37.5 parts of Cymel 325 (tradename, produced by Nihon

Cytec Industries Inc., a melamine resin, solids content: 80%) were uniformly mixed. Then, 26.2 parts of paste-form aluminum flake pigment (tradename "Alpaste MH-6601"; product of Asahi Chemical Industry Co., Ltd.; a paste with a pigment content of 65%, comprising aluminum flakes with a mean particle diameter of 14.5  $\mu\text{m}$ , a mean thickness of 0.21  $\mu\text{m}$  and a mean particle diameter/mean thickness ratio of 70, the aluminum flakes being dispersed in a petroleum solvent) was further added, followed by mixing. Next, Primal ASE-60 (tradename, product of Rohm & Haas Co., Ltd., a polyacrylic acid-based thickener), 2-(dimethylamino)ethanol, and deionized water were added thereto to thereby prepare aqueous luster thermosetting base coating composition (A-2) having a pH of 8.0, a coating composition solids content of 25%, and a viscosity of 40 seconds (Ford cup No. 4 at 20°C).

Aqueous luster thermosetting base coating composition (A-3)

Production Example 4

(Production of acrylic resin solution)

Five hundred and fifty parts of propylene glycol mono-n-propyl ether was introduced in a 4-liter flask, and the flask was heated to 115°C under a nitrogen stream. When the temperature reached 115°C, a monomer mixture obtained by dissolving 10 parts of azobisisobutyronitrile

in 350 parts of methyl methacrylate, 200 parts of n-butyl acrylate, 250 parts of 2-ethylhexyl methacrylate, 130 parts of 4-hydroxybutyl acrylate, 60 parts of acrylic acid, 10 parts of "Light Ester PM" (Note 1) was added to the flask over 3 hours, and the resulting mixture was aged for 2 hours. After completion of the reaction, the reaction product was neutralized with an equivalent amount of dimethylethanolamine. Then, 450 parts of propylene glycol mono-n-propyl ether was added to the flask, followed by the addition of dimethylethanolamine to adjust the pH to 7.5. Thereby, an acrylic resin solution in a yellow liquid form, having a glass transition temperature of 5°C, a weight average molecular weight of 45,000, and a solids content of 55% was obtained.

(Note 1) "Light Ester PM": tradename, product of Kyoeisha Chemical Co., Ltd., (2-methacryloiloxyethyl) acid phosphate.

#### Production Example 5

(Production of acrylic resin emulsion)

One hundred parts of deionized water, 2.5 parts of "Newcol 707SF" (product of Nippon Nyukazai Co., Ltd., an anionic emulsifier having polyoxyethylene chain; solids content: 30%), and 1 part out of the total amount of a monomer mixture (9 parts of styrene, 40 parts of n-butyl

acrylate, 40 parts of 2-ethylhexyl acrylate, 10 parts of 2-hydroxyethyl acrylate, and 1 part of methacrylic acid) were placed in a reactor, and mixed by stirring under a nitrogen stream, followed by the addition of 3 parts of 3% aqueous ammonium persulfate solution at 60°C. The resulting mixture was then heated to 80°C, and a pre-emulsion comprising 99 parts, i.e., the remaining portion, of the monomer mixture, 2.5 parts of "Newcol 707SF", 4 parts of 3% ammonium persulfate, and 100 parts of deionized water was added to the reactor over 4 hours using a metering pump. After addition, the resulting mixture was aged for 1 hour. Thereafter, 33 parts of deionized water was added thereto, followed by the addition of dimethylethanolamine to adjust the pH to 7.5. Thereby, an acrylic resin emulsion having a glass transition temperature of -44°C, a mean particle diameter of 0.1  $\mu$ m, and a solids content of 30% was obtained.

#### Production Example 6

(Production of urethane resin emulsion)

In a 4-liter flask, 115.5 parts of polybutylene adipate with a number average molecular weight of 2,000, 115.5 parts of polycaprolactone diol with a number average molecular weight of 2,000, 23.2 parts of dimethylolpropionic acid, 6.5 parts of 1,4-butanediol, and 120.1 parts of isophorone diisocyanate were placed and



reacted while stirring in a nitrogen gas atmosphere at 85°C for 7 hours to obtain a prepolymer with an NCO content of 4.0%. The prepolymer was then cooled to 50°C, and 165 parts of acetone was added to form a homogeneous solution. While stirring, 15.7 parts of triethylamine was added, and 600 parts of deionized water was added while maintaining the temperature at 50°C or lower. The obtained water dispersion was maintained at 50°C for 2 hours to complete the water extension reaction. Thereafter, the acetone was distilled off under reduced pressure at 70°C or lower, followed by the addition of triethylamine and deionized water to adjust the pH to 8.0. Thereby, a urethane resin emulsion having an acid value of 26 mgKOH/g, a solids content of 30%, and a mean particle diameter of 0.15  $\mu\text{m}$  was obtained.

#### Production Example 7

(Production of base coating composition)

To a stirring-mixing vessel, 26.2 parts of paste-form aluminum flake pigment (tradename "Alpaste MH-6601"; product of Asahi Chemical Industry Co., Ltd.; a paste with a pigment content of 65%, comprising aluminum flakes with a mean particle diameter of 14.5  $\mu\text{m}$ , a mean thickness of 0.21  $\mu\text{m}$  and a mean particle diameter/mean thickness ratio of 70, the aluminum flakes being dispersed in a petroleum solvent) and 40 parts of the acrylic resin solution

obtained in Production Example 4 were added. After 1 hour of stirring, 200 parts of the urethane resin emulsion obtained in Production Example 6 and 66.7 parts of the acrylic resin emulsion obtained in Production Example 5 were added and mixed. Then, 17.8 parts of "Primal ASE 60" (Note) were added thereto, and stirring was continued for another hour, followed by the addition of dimethylethanolamine to adjust the pH. Thereafter, deionized water was added thereto to thereby obtain a base coating composition with a solids content of 20%. When the viscosity and the pH of this base coating composition were measured in accordance with the method described in the specification, the viscosity was 1,000 mPa•sec, and the pH was 8.0.

(Note) "Primal ASE 60": tradename, product of Rohm & Haas Co., Ltd.; a polyacrylic acid-based thickener; acid value: 270 mgKOH/g; active ingredient: 28%.

#### Production Example 8

(Preparation of diluent)

As a diluent, a mixture of 970 parts of deionized water, 5 parts of "Laponite RD" (tradename, product of Rockwood Additives Limited, an inorganic thickener, synthetic hectorite,  $[\text{Si } 8 (\text{Mg } 5.34 \text{ Li } 0.66) \text{ O } 20 (\text{OH}) 4] \text{Na } 0.66$ ), and 25 parts of ethylene glycol monobutyl ether was used.

#### Production Example 9

Twenty-one parts of Bayhydur 3100 (tradename, a water-dispersible hexamethylene diisocyanate-based polyisocyanate; NCO content: 17.2%; product of Bayer MaterialScience), 78 parts of diethylene glycol monoethyl ether acetate, and 1 part of methyl orthoacetate were placed in a stainless steel beaker, and stirred with a glass rod to obtain a homogeneous mixture. Thereby, a curing agent was obtained.

#### Production Example 10

(Production of aqueous luster thermosetting base coating composition (A-3))

One hundred parts of the base coating composition obtained in Production Example 7 and 100 parts of the diluent obtained in Production Example 8 were mixed to obtain an aqueous luster thermosetting base coating composition (A-3).

#### Production of thermosetting clear coating composition (B)

##### Production Example 11

(1) A monomer mixture of 20 parts of acrylic acid, 20 parts of styrene, 40 parts of n-butyl acrylate and 20 parts of 4-hydroxy n-butyl acrylate was copolymerized in a standard manner to obtain a carboxy-

and hydroxy-containing acrylic resin with a number average molecular weight of 3,500, acid value of 86 mgKOH/g and hydroxy value of 78 mgKOH/g.

(2) A monomer mixture of 30 parts of glycidyl methacrylate, 20 parts of 4-hydroxy n-butyl acrylate, 40 parts of n-butyl acrylate and 20 parts of styrene was copolymerized in a standard manner to obtain an epoxy- and hydroxy-containing acrylic resin with a number average molecular weight of 3,000, epoxy content of 2.1 mmol/g and hydroxyl value of 78 mgKOH/g.

(3) A mixture of 50 parts of the carboxy- and hydroxy-containing acrylic resin obtained in (1) above, 50 parts of the epoxy- and hydroxy-containing acrylic resin obtained in (2) above, 1 part of an ultraviolet absorber (tradename "Tinuvin 900", product of Ciba-Geigy), 1 part of tetrabutylammonium bromide and 0.1 part of a surface conditioner (tradename "BYK-300", product of BYK-Chemie) was diluted with an aromatic hydrocarbon solvent (tradename "Swasol #1000", product of Cosmo Oil Co., Ltd.) to adjust the viscosity to 20 seconds (Ford cup #4, 20°C) and thereby obtain thermosetting clear coating composition (B-1).

#### Production of substrate

##### Production Example 12

A cationic electrodeposition coating composition

(tradename "Elecron 9400HB", product of Kansai Paint Co., Ltd.) was applied by electrodeposition to a degreased and zinc phosphate-treated steel sheet to a thickness of 25  $\mu\text{m}$  (when cured), and heat-cured at 170°C for 20 minutes. A polyester resin-based intermediate coating composition (tradename "Amilac Intermediate Coat, Gray", product of Kansai Paint Co., Ltd.) was applied by air spraying to the cured electrodeposition coating to a thickness of 35  $\mu\text{m}$  (when cured), heat-cured at 140°C for 20 minutes to obtain a substrate having an electrodeposition coating and intermediate coating.

#### Production of coated sheet

##### Experiment 1

Aqueous luster thermosetting base coating composition (A-2) obtained in Production Example 3 was applied in two stages to the substrate obtained in Production Example 12, using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.7 kg/cm<sup>2</sup>, gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, in such a manner that the thickness of the coating composition applied in each stage became about 3.5  $\mu\text{m}$  (when cured) and the total thickness of the coating composition applied in the two stages became 7  $\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The

solids content of the applied composition one minute after the application in each stage was 50%.

After the two stages of application, the applied composition was allowed to stand for 3 minutes and preheated at 80°C for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating layer of aqueous luster thermosetting base coating composition (A-2) to a thickness of 30  $\mu\text{m}$  (when cured), using a Minibell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.5  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, allowed to stand for 7 minutes, and heated at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of aqueous luster thermosetting base coating composition (A-2) and clear coating composition (B-1).

Aqueous luster thermosetting base coating composition (A-2) was applied in two stages over the cured coating layer of clear coating composition (B-1) using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.7  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75°C, in such a manner that the thickness of the coating composition applied in each stage became about 3.5  $\mu\text{m}$  (when cured) and the total thickness of the coating composition applied in the two stages became 7  $\mu\text{m}$  (when cured). The applied coating composition was allowed to

stand for 1 minute between the stages. The solids content of the applied composition one minute after the application in each stage was 50%.

After the two stages of application, the applied composition was allowed to stand for 3 minutes, and preheated at 80°C for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating layer of aqueous luster thermosetting base coating composition (A-2) to a thickness of 30  $\mu\text{m}$  (when cured), using a Minibell rotary electrostatic spray coater at 30,000 rpm, shaping pressure of 1.5  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, allowed to stand for 7 minutes and heated at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of aqueous luster thermosetting base coating composition (A-2) and clear coating composition (B-1).

A coated sheet was thus obtained in which a luster multilayer coating film was formed on a substrate by a four-coat two-bake method.

## Experiment 2

Aqueous luster thermosetting base coating composition (A-2) obtained in Production Example 3 was applied in two stages to the substrate obtained in Production Example 12, using a Metabell rotary

electrostatic coater at 30,000 rpm, shaping pressure of 1.7 kg/cm<sup>2</sup>, gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, in such a manner that the thickness of the coating composition applied in the first stage became about 5 µm (when cured), the thickness of the coating composition applied in the second stage became about 2.5 µm (when cured), and the total thickness of the coating composition applied in the two stages became 7.5 µm (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids content of the applied composition one minute after the application in the first stage was 45%. The solids content of the applied composition one minute after the application in the second stage was 60%.

After the two stages of application, the applied composition was allowed to stand for 3 minutes and preheated at 80°C for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating layer of aqueous luster thermosetting base coating composition (A-2) to a thickness of 30 µm (when cured), using a Minibell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.5 kg/cm<sup>2</sup>, gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, allowed to stand for 7 minutes and heated at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of aqueous luster thermosetting base coating



composition (A-2) and clear coating composition (B-1).

Aqueous luster thermosetting base coating composition (A-2) was applied in two stages over the cured coating layer of clear coating composition (B-1), using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of  $1.7 \text{ kg/cm}^2$ , gun distance of 30 cm, booth temperature of  $20^\circ\text{C}$  and booth humidity of  $75^\circ\text{C}$ , in such a manner that the thickness of the coating composition applied in each stage became about  $2.5 \text{ }\mu\text{m}$  (when cured) and the total thickness of the coating composition applied in the two stages became  $5 \text{ }\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids contents of the applied composition one minute after the application in the first and second stages were each 60%.

After the two stages of application, the applied composition was allowed to stand for 3 minutes, and preheated at  $80^\circ\text{C}$  for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating layer of aqueous luster thermosetting base coating composition (A-2) to a thickness of  $30 \text{ }\mu\text{m}$  (when cured) using a Minibell rotary electrostatic spray coater at 30,000 rpm, shaping pressure of  $1.5 \text{ kg/cm}^2$ , gun distance of 30 cm, booth temperature of  $20^\circ\text{C}$  and booth humidity of 75%. The applied composition was allowed to stand for 7 minutes, and heating was performed at  $140^\circ\text{C}$  for 30 minutes

to simultaneously cure the two uncured coating layers of aqueous luster thermosetting base coating composition (A-2) and clear coating composition (B-1).

A coated sheet was thus obtained in which a luster multilayer coating film was formed on a substrate by a four-coat two-bake method.

### Experiment 3

Aqueous luster thermosetting base coating composition (A-2) obtained in Production Example 3 was applied in five stages to the substrate obtained in Production Example 12, using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of  $1.7 \text{ kg/cm}^2$ , gun distance of 30 cm, booth temperature of  $20^\circ\text{C}$  and booth humidity of 75%, in such a manner that the thickness of the coating composition applied in each stage became about  $2 \text{ }\mu\text{m}$  (when cured), and the total thickness of the coating composition applied in the five stages became  $10 \text{ }\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids content of the applied composition one minute after the application in each of the stages was 50%.

After the five stages of application, the applied composition was allowed to stand for 3 minutes and preheated at  $80^\circ\text{C}$  for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating

layer of aqueous luster thermosetting base coating composition (A-2) to a thickness of 30  $\mu\text{m}$  (when cured), using a Minibell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.5  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, allowed to stand for 7 minutes and heated at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of aqueous luster thermosetting base coating composition (A-2) and clear coating composition (B-1).

Aqueous luster thermosetting base coating composition (A-2) was applied in five stages over the cured coating layer of clear coating composition (B-1), using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.7  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75°C, in such a manner that the thickness of the coating composition applied in each stage became about 2  $\mu\text{m}$  (when cured) and the total thickness of the coating composition applied in the five stages became 10  $\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids content of the applied composition one minute after the application in each of the stages was 50%.

After the five stages of application, the applied composition was allowed to stand for 3 minutes, and preheated at 80°C for 10 minutes. Clear coating

composition (B-1) was applied over the uncured coating layer of aqueous luster thermosetting base coating composition (A-2) to a thickness of 30  $\mu\text{m}$  (when cured) using a Minibell rotary electrostatic spray coater at 30,000 rpm, shaping pressure of 1.5  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%. The applied composition was allowed to stand for 7 minutes, and heating was performed at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of aqueous luster thermosetting base coating composition (A-2) and clear coating composition (B-1).

A coated sheet was thus obtained in which a luster multilayer coating film was formed on a substrate by a four-coat two-bake method.

#### Experiment 4

The procedure of Experiment 1 was followed except that each of the first and third coating layers was formed by applying aqueous luster thermosetting base coating composition (A-2) in a single stage to a thickness of about 7  $\mu\text{m}$  (when cured), to obtain a coated sheet in which a luster multilayer coating film was formed on a substrate by a four-coat two-bake method.

#### Experiment 5

Aqueous luster thermosetting base coating

composition (A-2) was applied in two stages to the substrate obtained in Production Example 12, using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of  $1.7 \text{ kg/cm}^2$ , gun distance of 30 cm, booth temperature of  $20^\circ\text{C}$  and booth humidity of 75%, in such a manner that the thickness of the coating composition applied in each stage became about  $6 \text{ }\mu\text{m}$  (when cured), and the total thickness of the coating composition applied in the two stages became  $12 \text{ }\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids contents of the applied composition one minute after the application in the first and second stages were each 40%.

After the two stages of application, the applied composition was allowed to stand for 3 minutes and preheated at  $80^\circ\text{C}$  for 10 minutes. Clear coating composition (B-1) was applied to the uncured coating layer of aqueous luster thermosetting base coating composition (A-2) to a thickness of  $30 \text{ }\mu\text{m}$  (when cured), using a Minibell rotary electrostatic spray coater at 30,000 rpm, shaping pressure of  $1.5 \text{ kg/cm}^2$ , gun distance of 30 cm, booth temperature of  $20^\circ\text{C}$ , and booth humidity of 75%. The applied composition was allowed to stand for 7 minutes, and heating was performed at  $140^\circ\text{C}$  for 30 minutes to simultaneously cure the two uncured coating layers of aqueous luster thermosetting base coating composition (A-

2) and clear coating composition (B-1).

A coated sheet was thus obtained in which a luster multilayer coating film was formed on a substrate by a two-coat one-bake method.

#### Experiment 6

The procedure of Experiment 4 was followed except that aqueous luster thermosetting base coating composition (A-2) was applied in three stages, in such a manner that the thickness of the coating composition applied in each stage became about 8  $\mu\text{m}$  (when cured), about 4  $\mu\text{m}$  (when cured), and about 4  $\mu\text{m}$  (when cured), to obtain a coated sheet in which a luster multilayer coating film was formed on a substrate by a two-coat one-bake method.

#### Experiments 7 to 12

The coated sheets of Experiments 7 to 12 were obtained in the same manner as in Experiments 1 to 6, except that a mixture, in which aqueous luster thermosetting base coating composition (A-3) and the curing agent obtained in Production Example 9 were mixed in a mass ratio of 10/1 (the base coating composition/curing agent) before application and diluted with water to a solids content of about 40%, was used in place of aqueous luster thermosetting base coating

composition (A-2).

#### Performance evaluation tests

The coated sheets obtained in Experiments 1 to 12 were tested for density of texture and flip-flop property by the following methods.

Density of texture: The highlight of the coating surface of each coated sheet was observed by the naked eye, and evaluated according to the following criteria. A: The coating surface was only slightly grainy and had a highly dense texture; B: The coating surface was very grainy and had a poor density of texture.

As another evaluation of the density of texture, the HG (Highlight Graininess) value of the coating surface of each coated sheet was measured using a micro-brilliance measuring instrument (product of Kansai Paint Co., Ltd.). The micro-brilliance measuring instrument is equipped with a light source, a CCD (Charge Coupled Device) camera and an image analyzer, and is disclosed in Japanese Unexamined Patent Publication No. 2001-221690.

The HG value is a parameter of micro-brilliance obtained by the microscopic observation of a coating surface, and indicates the graininess of the highlight of the coating surface. The HG value is calculated as follows.

First, the coating surface is photographed with

a CCD camera at a light incidence angle of  $15^\circ$  and receiving angle of  $0^\circ$ , and the obtained digital image data (two-dimensional brilliance distribution data) is subjected to two-dimensional Fourier transformation to obtain a power spectrum image. Subsequently, the spatial frequency area corresponding to graininess is extracted from the power spectrum image, and the obtained measurement parameter is converted to an HG value from 0 to 100 that has a linear relation with graininess.

An HG value of 0 indicates no graininess of the luster pigment at all, and an HG value of 100 indicates the highest possible graininess of the luster pigment.

Flip-flop property: The highlight and shade of the coating surface of each coated sheet were observed by the naked eye, and evaluated according to the following criteria. A: A large difference in brightness between the highlight and shade; B: A small difference in brightness between the highlight and shade; C: Almost no difference in brightness between the highlight and shade.

Further, using a multi-angle spectrophotometer (tradename "MA68II", product of X-Rite in the U.S.), the color of the coating surface of each coated sheet was determined, and the reflectance at receiving angles of  $15^\circ$  and  $110^\circ$  from the regular reflection light was measured at a light incidence angle of  $45^\circ$ . The ratio of the reflectance at a receiving angle of  $15^\circ$  to that at a



receiving angle of  $110^\circ$  (FF value) was calculated. The higher the FF value, the higher the flip-flop property.

### 3. Results

Tables 1 and 2 show the results of the evaluation tests of density of texture and flip-flop property.

[Table 1]

Experiment		1	2	3	4	5	6
Density of texture	Naked eye observation	A	A	A	B	B	B
	HG value	45	47	47	56	57	58
Flip-flop property	Naked eye observation	A	A	A	B	C	C
	FF value	1.8	1.8	1.8	1.4	1.3	1.3

[Table 2]

Experiment		7	8	9	10	11	12
Density of texture	Naked eye observation	A	A	A	B	B	B
	HG value	45	47	46	56	58	58
Flip-flop property	Naked eye observation	A	A	A	B	C	C
	FF value	1.8	1.8	1.8	1.4	1.3	1.3

### 4. Analysis

The coating film obtained by the method comprising repeating the step of applying aqueous luster thermosetting base coating composition (A-2) (steps (1) and (3)), and the step of applying a thermosetting clear coating composition (steps (2) and (4)), wherein in steps (1) and (3), the aqueous luster thermosetting base coating composition is applied in two to five stages, in such a manner that the thickness of the base coating composition applied in each stage becomes 0.3 to 5  $\mu\text{m}$  when cured (Experiments 1 to 3) showed a highly dense texture and excellent flip-flop property.

Comparatively, when the base coating composition was applied in three stages at each thickness of 8  $\mu\text{m}$ , 4  $\mu\text{m}$  and 4  $\mu\text{m}$ , and the step of applying the base coating composition and the step of applying the clear coating composition were not repeated (Experiment 6), although each thickness of the base coating composition applied in the second and third stages was relatively as thin as 4  $\mu\text{m}$ , the obtained coating film showed significantly inferior dense texture and flip-flop property.

Experiment 4 is different from Experiment 5 in that each of the base coating composition and the clear coating composition was repeatedly applied over a coating film consisting of base coating composition layers and clear

coating composition layers; however, the coating film obtained in Experiment 4 showed almost no improvement in the dense texture and flip-flop property.

Experiment 6 is different from Experiment 5 in that the number of the stages of applying the base coating composition was increased from two to three, and the thicknesses of the coating composition applied in the second and third stages were made thinner; however, the results of the flip-flop property showed no difference, and the dense texture was an undesirably high value.

Results similar to the above were obtained when aqueous luster thermosetting base coating composition (A-3) was used.

Specifically, the coating film obtained by the method comprising repeating the step of applying an aqueous luster thermosetting base coating composition (steps (1) and (3)), and the step of applying a thermosetting clear coating composition (steps (2) and (4)), wherein in steps (1) and (3), the aqueous luster thermosetting base coating composition is applied in two to five stages, in such a manner that the thickness of the base coating composition applied in each stage becomes 0.3 to 5  $\mu$ m when cured (Experiments 7 to 9) showed a highly dense texture and

excellent flip-flop property.

Comparatively, when the base coating composition was applied in three stages at each thickness of 8  $\mu\text{m}$ , 4  $\mu\text{m}$  and 4  $\mu\text{m}$ , and the step of applying the base coating composition and the step of applying the clear coating composition were not repeated (Experiment 12), although each thickness of the base coating composition applied in the second and third stages was relatively as thin as 4  $\mu\text{m}$ , the obtained coating film showed significantly inferior dense texture and flip-flop property.

Experiment 10 is different from Experiment 11 in that each of the base coating composition and the clear coating composition was repeatedly applied over a coating film consisting of base coating composition layers and clear coating composition layers; however, the coating film obtained in Experiment 10 showed almost no improvement in the dense texture and flip-flop property.

Experiment 12 is different from Experiment 11 in that the number of the stages of applying the base coating composition was increased from two to three, and the thicknesses of the coating composition applied in the second and third stages were made thinner; however, no improvements were observed in the results of the flip-flop

property and the dense texture.

I, the undersigned, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: June 10, 2011

Tsukasa Fujieda

Tsukasa Fujieda